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Photochromism of 1,2-Dihydroquinolines

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Jaroslav Kolc, Ralph S. Becker

Photochromism of 1,2-Dihydroquinolines

Sir:

As a part of our continuing investigation of the spectroscopy and primary photochemical processes of molecules,[1] we wish to report photochemistry (photochromism) of the 1,2-dihydroquinolines. Their colorless solid solutions in EPA[2] at −196° develop color upon irradiation with ultraviolet light (1-kW Hg–Xe source, Corning glass filter 9863 transmitting approximately in the region of 250–390 nm).

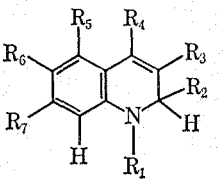
The colored form can be eradicated thermally and the process can be repeated several times. Thus far, we have investigated six dihydroquinolines; five of them exhibited photochromic behavior. They are listed in Table I.[3]

(1) For example, see R. S. Becker and J. Kolc, *J. Phys. Chem.*, **72**, 997 (1968), and references therein; A. Santiago and R. S. Becker, *J. Amer. Chem. Soc.*, **90**, 3654 (1968); R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969), and references therein.

(2) Ethyl ether, isopentane, and ethyl alcohol in volume ratio of 5:5:2, respectively.

(3) Compound **1** was synthesized in this laboratory according to H. Rupe, R. Paltzer, and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937), and recrystallized several times from ethanol. Compounds **3** and **4** were purchased from Aldrich Chemical Co.; compounds **2** and **5** (and also **1**) were generously donated by Dr. F. D. Popp, Clarkson College of Technology, Potsdam, N. Y. Compound **6** was a kind gift from Drs. H. O. Huisman and W. N. Speckamp, University of Amsterdam, The Netherlands.

Table I



Compound no.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	Colored form in EPA matrix at 77°K
1	COC_6H_5	CN	H	H	H	H	H	Brownish red
2	$CO_2C_2H_5$	CN	H	H	H	H	H	Orange
3	$CO_2C_2H_5$	OC_2H_5	H	H	H	H	H	Pink
4	CN	OH	H	H	H	H	H	Blue
5	COC_6H_5	CN	H	H	Benzo		H	Yellow
6	$SO_2C_6H_4CH_3$	H	CN	OCH_3	H	H	OCH_3	None

Compound **3** was subjected to the three irradiation–thermal eradication cycles. The total reversibility after the three cycles was better than 99% as determined by monitoring the absorption of the uncolored form in the region 280–310 nm. Similarly, compounds **1** and **5** were cycled five times with the complete disappearance of the visible band after each cycle. Reversibility was 97–98% per cycle. In the cases the of compounds **1** and **5**, there is some side reaction in addition to the reversible photochromic process. This is responsible for the gradual development of an additional band with an onset in the 370–400-nm region. The reversibility of compounds **2** and **4** was considerably lower than those considered above.

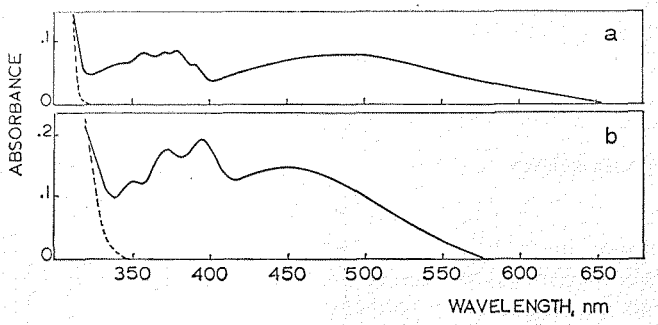
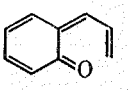


Figure 1. Absorption spectra of colored forms (——) of: (a) 1-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (1.2×10^{-3} *M* at 20° in EPA); (b) 1-benzoyl-2-cyano-1,2-dihydroquinoline (5.7×10^{-4} *M* at 20° in EPA). All spectra were taken in 2-mm Suprasil cells at −196°, irradiated 20 min with 1-kW Hg–Xe source at −196°; colorless forms before irradiation, – – – –.

The colored forms of dihydroquinolines **2** and **5** persist upon melting of the EPA matrix and warming up to room temperature, at which temperature they stay for some time. Some of the compounds (*e.g.*, **1**, **2**, and **5**) can be converted to their colored forms in liquid solution at −75°, and compound **2** at temperatures above 0°. Photochromism of the 1,2-dihydroquinolines seems to depend strongly upon the presence and nature of the substituents in positions 1 and 2; see Table I. Thus, compound **6** is not convertible to a colored form, and its first absorption band stays virtually unchanged upon prolonged irradiation. This effect of substituents is being studied further.

Absorption spectra of the colored forms of all compounds investigated show a broad band in the visible region and a more intense, usually structured band in the region 320–400 nm. Examples are given in Figure 1. A striking similarity exists with the absorption spectra of the colored forms of chromenes;[4] we have shown the structure of the colored form[5] to be **7**. This



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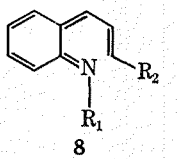

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indicates the strong possibility of a parallel structure **8** for the colored form of the 1,2-dihydroquinolines. A more detailed investigation of the photochemistry and spectroscopy of the dihydroquinolines is in progress.

Acknowledgment. This research was supported by the National Aeronautics and Space Administration, Grant NGR 44-005-091.

(4) R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, **88**, 5931 (1966); J. Kolc and R. S. Becker, submitted for publication.
(5) J. Kolc and R. S. Becker, *J. Phys. Chem.*, **71**, 4045 (1967).

Jaroslav Kolc, Ralph S. Becker
Department of Chemistry, University of Houston
Houston, Texas 77004
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